PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
(Case No. 98.162)

In re Application of:

DeGendt, et al.

Serial No.: 09/022,834

Filed: February 13, 1998

For: Method For Removing Organic Contaminants From A A Semiconductor Surface

Group Art Unit: 1746

Examiner: Ahmed

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Commissioner for Patents
Washington, DC 20231

DECLARATION OF STEFAN DEGENDT PURSUANT TO 37 C.F.R. § 1.132

#14
8-29-01

I, Stefan De Gendt, declare as follows:

1. I am a co-inventor of the subject matter of the above-identified patent application.

2. I received my PhD of Science in January 1996.

3. I hold the position of researcher at IMEC vzw, where I have been employed since February 1996.

4. There is a substantial difference between the removal of metallic contaminants and the removal of organic contaminants (and especially the removal of organic contaminants resulting from a previous lithographic step, and more especially the removal of the latter species/residues after a prior etch and (dry) strip process).

5. A typical wet cleaning sequence is SC1 step and then SC2 step. The SC1 step is typically an alkaline oxidizing step, used to remove particles in general, but is prone to introducing metallic contamination, requiring a further process step (e.g., SC2 step) The SC2 step is typically an acid oxidizing step, used to remove metallic species. The cleaning from the SC1 and SC2 steps is surface (monolayer) cleaning. This cleaning sequence is generally known as an RCA clean and has been introduced by Werner Kern 'RCA Rev. 31, 1970, p.187.

6. When thicker (visible) layers or residues must be removed, such as a layer of organic photoresist, at least extra processing steps are added. Typically, the sequence is as follows: SPM (sulphuric peroxide mixture) step, then diluted HF step, then SC1 step, and then SC2 step. SPM is a very oxidizing substance which very aggressively removes organic contaminants (such as those caused by a previous lithographic step). The SPM step is typically followed by a step in which diluted HF is applied. After the diluted HF step, the SC1 and SC2 steps are applied to further clean the substrate.

7. According to Werner Kern in J. Electrochem. Soc. Vol. 137, 1990, p. 1888 when discussing the above mentioned sequence, the following is stated:

> A preliminary clean-up treatment with a hot H2SO4-H202 mixture (2:1vol) can be used advantageously for grossly contaminated wafers having visible residues, such as photoresist layers. Another step, not noted in the original paper (see 5), concerns an etch in HF solution for bare silicon wafers ... A silicon surface that was exposed to HF is highly reactive and immediately attracts particles and organic contaminants from solutions, DI water and the ambient air. Contrary to SC-1, the subsequent SC-2 solution, which has no surfactant activity, will not eliminate these contaminants.'

(Emphasis added). In summary, not every mixture of an anorganic acid (e.g. HCl) and hydrogen peroxide are capable of removing organic contaminants from silicon substrates.

8. Using fluid comprised of water, ozone and an additive acting as a scavenger avoids the need for using, for example, the substance of the sulphuric peroxide mixture. This allows for a much more environmentally friendly method of processing.

9. When using fluid comprised of water, ozone and an additive acting as a scavenger, hydrogen peroxide is not interchangeable with ozone. Ozone is much more environmentally friendly than hydrogen peroxide. Moreover, the reactivity of ozone is much higher than that of hydrogen peroxide. Specifically, in order to provide the necessary reactivity in a hydrogen peroxide mixture, the concentration of the hydrogen peroxide are typically greater than 10% whereas for the equivalent reactivity in an ozone mixture, the concentration of ozone is in the parts per million (ppm) range. Finally, ozone is much cheaper to use than hydrogen peroxide. As discussed previously, the concentration of hydrogen peroxide must be above a certain percentage in order to achieve the desired reactivity. Over time, use of the bath decreases the concentration of the hydrogen peroxide, requiring the replacement of the bath or the addition of hydrogen peroxide. By contrast, ozone need only be bubbled up in the mixture, making processing significantly easier.

10. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of the Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Further the declarant sayeth not.

Respectfully submitted,

23 AUGUST 2001
Date

Stefan DeGendt